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A Computational Approach for the Rational Design of Bimetallic Clusters for Ethanol Formation from Syn-gas

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Activation of CO on Metal Clusters: Tools for Ab Initio based Models of Reactions and Surface Diffusion Phenomena

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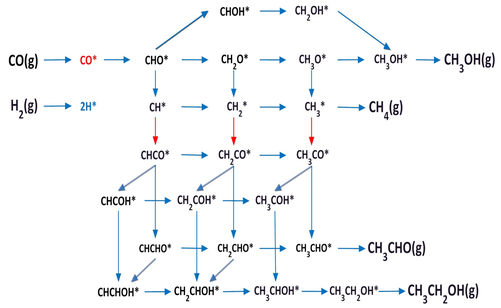
1. Background

The catalytic synthesis of ethanol from syn-gas ($2CO + 4H_2 \rightarrow C_2H_5OH + H_2O$) is important due to increased demand for alternative, renewable energy sources. A major challenge associated with this route is an inability to find a low-cost catalyst that promotes the proper combination of CO dissociation and CO insertion steps, so as to yield ethanol as the primary reaction product. Bimetallic catalysts, in which one metal promotes hydrocarbon production and the other oxygenate production, may exhibit a synergistic effect that can facilitate the formation of ethanol. As many bimetallic combinations are possible, a fundamental theoretical investigation is essential to shed light onto the complex reaction mechanism from syn-gas to ethanol. This analysis will enable a more complete computational combinatorial screening of catalysts.



Catalytic Activity for CO Hydrogenation

Cr	Mn	Fe	Co	Ni	Cu
Mo	Tc	Ru	Rh	Pd	Ag
W	Re	Os	Ir	Pt	Au

Syngas Products
- hydrocarbons
- oxygenates
- ethanol

2. Materials and Methods

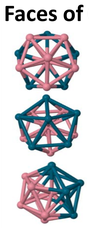
All electronic structure optimizations were performed with Jaguar 7 (Schrodinger), using the unrestricted spin DFT formalism at the B3LYP/LACVP** level of theory. Reaction pathways and transition states (TS) were mapped out using climbing image nudged elastic band method (CI-NEB) coupled with the quadratic synchronous transit (QST) method implemented in Jaguar. All final transition state structures had exactly one imaginary frequency. Microkinetic models were built based on transition-state theory (TST) formalism at experimental conditions to evaluate selectivity of final products. A more recent functional, M06/LACVP**, was used to correct for dispersion interactions that are poorly addressed using the B3LYP functional.

3. Result and Discussion

3.1. Ethanol formation studies on CoPd Cluster

The icosahedral Co_7Pd_6 cluster was selected to model the active sites (structures based on work by Aguilera). Density Functional Theory (DFT) simulations and Bronsted-Evans-Polanyi (BEP) relations were used to map out the full reaction mechanism. Rate data was calculated from microkinetic models, considering all reaction steps and the diffusion of intermediate species among the Co_3, Pd_3 and mixed CoPd sites.

Faces of Co_7Pd_6 Cluster



5 Co only

5 Pd only

10 mixed Co-Pd

3.1.1 BEP relationships

A total of 37 surface reactions occuring on three distinct surface site types were included in our mechanism for ethanol formation from syn-gas, yielding more than 100 possible surface reaction steps for which to calculate rate constants. To more rapidly solve this computationally intensive problem, we judiciously employed various scaling methods.

A widely used scaling method for estimating activation energies is the Bronsted-Evans-Polanyi (BEP) relation, which linearly correlates the transition state energy of an elementary step to the reaction enthalpy of that step. Thus, a task of considerable computational cost (transition state searching) can be replaced with two moderate computations (energy minimizations of the reactant and product).

To apply the BEP relation to the Co-Pd binary cluster, the transition state energies of these steps are plotted against reaction energies, by which a linear relationship is deduced.

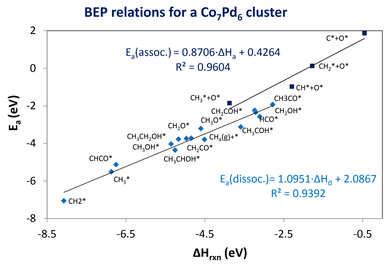


Table 1. Relative Selectivity(%) for Simulated and Experimental Systems

	Methane	Methanol	Acetaldehyde	Ethanol
Microkinetic model on CoPd cluster– no diffusion between sites at 523 K, P_{CO}= 0.6 atm, P_{H2}= 1.2 atm				
Co sites only	**99.99**	0.001	1.507	0.020
Pd sites only	7.11	**92.88**	0.002	0.000
CoPd sites only	40.479	0.553	**58.801**	0.167
Experiment data at 230 °C, P_{CO}= 0.6 atm, P_{H2}= 1.2 atm				
Co(5wt%)/Al_2O_3	**97.2**	2.0	0.6	0.2
Pd(5wt%)/Al_2O_3	20.0	**79.7**	0.0	0.3

3.2. Microkinetic model

Microkinetic modeling was used to examine the intrinsic nature of the three distinct catalytic sites. The pseudo-steady state hypothesis (PSSH) is applied to calculate surface concentrations of intermediate species. We find good agreement of reaction selectivity between our model and experiments (Table 1). It is interesting to note that the C2 oxygenate is only formed on the CoPd sites. We find a universal reaction mechanism exists on all three sites, as shown below. Diffusion behavior was examined for important surface bound intermediates. The overall reaction rate and relative selectivity are estimated under typical experimental conditions (P_{CO}=4atm, P_{H2}=8atm, 523K). The selectivities resulting from our microkinetic model with diffusion are presented in Table 2.

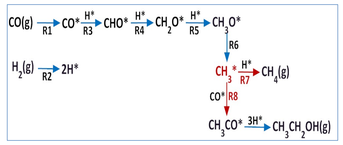
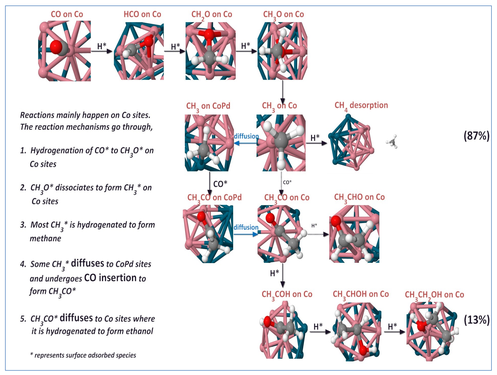
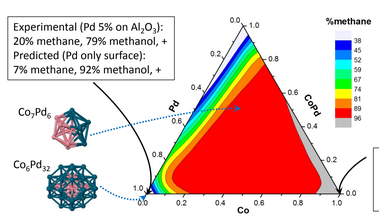


Table 2. Selectivity from microkinetic model with diffusion (T= 523K, P_{CO}= 4atm, P_{H2}= 8atm)

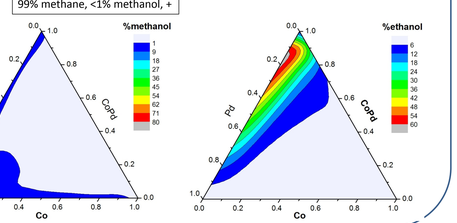
Selectivity (%)	Methane	Methanol	Acetaldehyde	Ethanol
Co sites	**84.735**	0.003	0.135	**13.033**
Pd sites	0.000	0.000	0.000	0.009
CoPd sites	2.086	0.000	0.000	0.000

To conclude our microkinetic modeling study, the overall reaction mechanism chart for ethanol formation on the Co_7Pd_6 cluster is presented. The reactions proceed on the Co sites of the cluster. CO insertion into the metal-carbon bonds of adsorbed methyl groups is the primary pathway to produce C_2 oxygenates. Methane is the major product (87%). Some ethanol (13%) can also form on Co sites via the diffusion of CH_3 and CH_3CO species between Co sites and CoPd sites, thus facilitating CO insertion reactions.



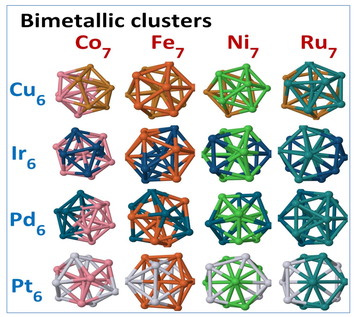


The surface fractional coverage of catalyst sites is altered to study the effect of catalyst composition on the overall selectivity. It is noted methane will likely be the major product on catalysts consisting of Co and Pd metals.



It is also likely to have methanol production if the catalyst is very rich in a Pd phase. To promote the selectivity of C2 oxygenates, a high surface coverage of mixed CoPd sites is required.

4. 13-atom bimetallic clusters

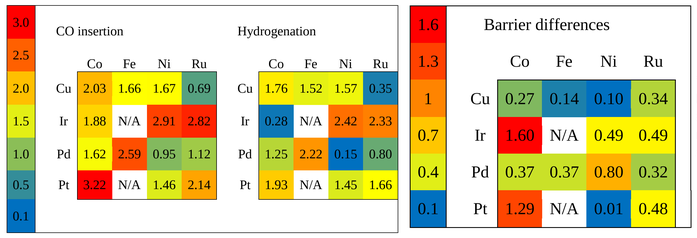


For each 50/50 mixed bimetallic cluster, 30 different configurations were optimized to get the most stable conformer, shown here.

The 16 optimized clusters were modeled as catalyst in ethanol formation reactions.

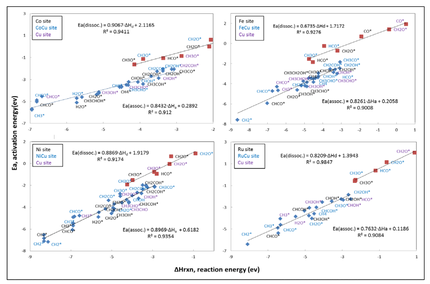
From the CoPd work, it is observed that the difference in reaction barriers for CO insertion and hydrogenation of CH_3* plays a critical role in ethanol selectivity. For the 16 combinations of bimetallic clusters, these two reactions are explicitly calculated using the CI-NEB/QST method.

The reaction barriers (eV) are summarized below.

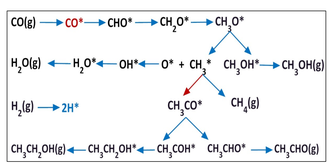


* For FeIr and FePt, the 13-atom cluster is not a stable structure.

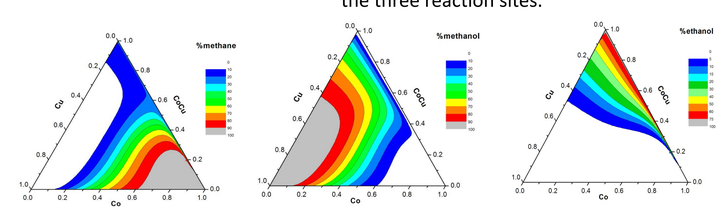
From the calculated barriers, it is suggested that the bimetallic compositions of NiPt, CoCu, FeCu, NiCu, and RuCu are promising candidates as catalysts for ethanol formation reactions. To verify these assertions, BEP relations were constructed for the four copper based clusters. The selectivity results on individual sites were obtained from microkinetic modeling at P_{CO}=3.33 bar, P_{H2}= 6.66 bar, 523K.



Selectivity (%)	Methane	Methanol	Acetaldehyde	Ethanol
CoCu cluster				
Co site	**99.9**	0.0	0.0	0.1
Cu site	23.7	**63.5**	12.8	0.0
CoCu site	3.6	0.0	0.2	**96.2**
FeCu cluster				
Fe site	**97.1**	0.0	0.3	2.6
Cu site	0.0	**100.0**	0.0	0.0
FeCu site	**99.7**	0.0	0.0	0.3
NiCu cluster				
Ni site	**100.0**	0.0	0.0	0.0
Cu site	42.1	**57.8**	0.0	0.0
NiCu site	10.8	0.0	1.8	**87.5**
RuCu cluster				
Ru site	**90.5**	6.9	0.0	2.6
Cu site	0.3	**99.7**	0.0	0.0
RuCu site	7.7	**74.6**	0.0	17.6



The Co_7Cu_6 cluster shows characterization for ethanol formation, which suggests the bimetallic combinations of Co and Cu could be potential catalysts for this reaction. The microkinetic model on the Co_7Cu_6 cluster was extended to different metal compositions by altering surface coverage of the three reaction sites.



It is found to have significant ethanol production the majority of the catalytic surface needed to be the mixed CoCu site or the combination of the mixed CoCu site and the Co site. This result suggests the atomic-level design of catalysts and novel synthesis method is necessary to increase surface coverage of the mixed metal sites.

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